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Calcd for $NbC_{12}H_{21}Cl_2$: C, 43.79; H, 6.43; Cl, 21.54. Found: C, 43.81; H, 6.64; Cl, 21.40.

Preparation of $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$. A solution of $Nb(\eta^5\text{-}C_5Me_5)Me_2Cl_2$ (2.3 g, 7.0 mmol) in 70 mL of toluene was added to a glass pressure vessel and stirred under H_2 (35 psi) for 14 h. The green mixture was filtered and the filtrate concentrated in vacuo. Pentane was added, and the solution was cooled to −30 °C to give green crystals of $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$: 1.4 g (66%); ^1H NMR (C_6H_6) δ 2.27 (s, C_5Me_5). Anal. Calcd for $NbC_{10}H_{15}Cl_2$: C, 40.17; H, 5.37; Cl, 23.71. Found: C, 40.09; H, 5.25; Cl, 23.55.

Preparation of $Nb(\eta^5\text{-}C_5Me_5)(3\text{-hexyne})Cl_2$. $[Nb(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (150 mg, 0.25 mmol) was dissolved in toluene (10 mL), and 3-hexyne (200 μL, 7.3 equiv) was added. After 15 h, the solvent was removed from the purple solution in vacuo and the residue recrystallized from minimal pentane to give $Nb(\eta^5\text{-}C_5Me_5)(3\text{-hexyne})Cl_2$: 160 mg (83%); ^1H NMR (C_6D_6) δ 2.95 (q, 4, J_{HH} = 7.5 Hz, CH_2CH_3), 1.66 (s, 15, C_2Me_5), 1.17 (t, 6, J_{HH} = 7.5 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 217.7 (acetylenic C), 121.0 (C_5), 28.9 (C_5Me_5), 14.4 (CH_2CH_3), 11.8 (CH_2CH_3); IR (Nujol) 1725 cm^{-1} ($\nu_{C\equiv C}$). Anal. Calcd for $NbC_{16}H_{25}Cl_2$: C, 50.42; H, 6.61; Cl, 18.60. Found: C, 50.32; H, 6.64; Cl, 19.53.

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Bis(acetylacetonato)fluorovanadium(III), $VF(C_5H_7O_2)_2$. Synthesis of a Novel Neutral Compound of Vanadium(III) from Vanadium(V)

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The tripositive state of vanadium is one of its unusual oxidation states, mainly owing to the instability of vanadium(III) compounds. Predominant among the known compounds of vanadium(III) are those derived from vanadium(III) trihalides.[1] Trivalent vanadium also forms some neutral mixed-ligand complexes of the types VL_3X_3 and VL_2X_3, with L being a unidentate ligand and X a halide, particularly chloride. The neutral complex of V^{3+} of the type $V(L\text{-}L')_2X$, with L-L′ being a bidentate mononegative ligand, does not appear to have any reported example in the literature. Moreover, reports on the syntheses of trivalent vanadium compounds from V^{5+} through chemical reduction are rather scanty. In a continuation of our studies on the synthesis and structural assessment of fluoro[2] and mixed fluoro[3,4] compounds of vanadium, we have developed a method for the synthesis of a new neutral complex of vanadium(III), $VF(acac)_2$, which we have achieved by a two-step electron-transfer process starting from vanadium pentoxide. In this report we present an account of the synthesis, characterization, and structural assessment of the title compound.

Experimental Section

All chemicals were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method. $Hg[Co(NCS)_4]$ was the calibrant.

The mass spectra were recorded on a Varian MAT CH-5 spectrometer using a direct-insertion probe to introduce the sample directly into the ion source without any prior heating. The operation conditions were as follows: electron energy 70 eV (1 eV $\simeq 1.6 \times 10^{-19}$ J); source temperature 50, 100, and 150 °C; resolution 10 000; accelerating voltage 8 kV. The mass spectrometric observations were made with the field of ionizing current being maintained sufficiently strong to trap primary ions.

Synthesis of Bis(acetylacetonato)fluorovanadium(III), $VF(C_5H_7O_2)_2$. A suspension of 2.0 g (11 mmol) of V_2O_5 in 10 cm^3 of water was treated with 2.2 cm^3 (44 mmol) of 40% hydrofluoric acid. The mixture was warmed on a steam bath with stirring for 10–15 min and then cooled followed by filtration to remove any undissolved impurity. The clear solution was cooled in an ice bath, and 99% hydrazine hydrate solution was added dropwise with occasional stirring. The solution first turned blue. The addition of hydrazine hydrate was continued until a blue crystalline compound ceased to appear, with the mother liquor becoming very faint in color. The blue compound was separated by centrifugation and dried on a filter paper and finally in vacuo. The compound was identified as $N_2H_5VOF_3$, yield 1.6 g (92%). Anal. Calcd for $N_2H_5VOF_3$: N, 17.85; H, 3.19; V, 32.47; F, 36.31. Found: N, 17.91; H, 3.14; V, 32.5; F, 36.1. Molar conductance (water): 130 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (302 K): 1.51 μ_B (1 $\mu_B \simeq 0.927 \times 10^{-23}$ A m^2). IR: 970 (ν_{V-O}), 500 cm^{-1} (ν_{V-F}).

In a further experiment, starting from comparatively higher amounts of the reagents and after purging the reaction vessel with argon, the evolved gas was first passed through a dry sodium hydroxide tower and then over heated (~450 °C) magnesium. The magnesium nitride thus formed was treated with water and tested for the liberation of ammonia.

The blue hydrazonium oxotrifluorovanadate(IV), $N_2H_5VOF_3$ (1.6 g, 10.2 mmol), dissolved in about 8 cm^3 of water, and acetylacetone (10 g, 100 mmol) were placed in a small polyethylene conical flask, the neck of which was plugged with cotton wool, the whole was heated on a steam bath for ca. 1 h, and a dark blue-green solution was obtained. On cooling, blue-green crystals of bis(acetylacetonato)fluorovanadium(III), $VF(acac)_2$, were formed, which were removed from the flask and dried on a filter paper. The compound was recrystallized by dissolving in hot benzene followed by addition of petroleum ether (bp 40–60 °C) until the solution was cloudy: yield of $VF(C_5H_7O_2)_2$ 2.5 g (84.7% on the basis of V_2O_5); mp 246–248 °C. Anal. Calcd for $C_{10}H_{14}VO_4F$: C, 44.78; H, 5.27; V, 18.99; F, 7.1. Found: C, 44.32; H, 5.6; V, 18.4; F, 6.9. Magnetic moment (302 K): 2.77 μ_B. M_r: calcd, 268; found (mass spectrum), 268.

Workup of the mother liquor, obtained after isolation of $VF(acac)_2$, afforded a small amount of $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2C\text{-}HCH(CH_3CO)_2$, being the oxidation product of acetylacetone.

Elemental Analyses. Carbon, hydrogen, nitrogen, and fluoride analyses were obtained from Amdel, Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia.

Vanadium was estimated volumetrically by titration with standard potassium permanganate. The compounds were first decomposed, and vanadium was oxidized to vanadium(V). A near-boiling vanadium(V) solution was treated with a stream of sulfur dioxide for ca. 10 min and then with a rapid stream of carbon dioxide to expel any excess of sulfur dioxide. The vanadium(V) solution was then cooled to ca. 80 °C and titrated with standard potassium permanganate.[5] Fluoride was also determined by precipitating as lead chloride fluoride, PbClF, and chloride was estimated by Volhard's method, from which the fluoride content was calculated.[6]

Results and Discussion

Vanadium pentoxide readily reacts with 40% hydrofluoric acid and an excess of hydrazine hydrate to yield a blue crystalline compound. The compound is soluble in water, and the results of elemental analyses suggest the atom ratio N:H:V:F as 2:5:1:3. The infrared spectrum of the compound showed a strong band at 970 cm^{-1}, indicating the presence of a V–O multiple bond, and was accordingly assigned[7] to ν_{V-O}. The band at 500 cm^{-1} has been assigned as the ν_{V-F} mode,

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Table I. Mass Spectrometric Data for VF(acac)$_2$

Major Peaks

assignts	*m/z*	intens, %
$[VF(C_5H_7O_2)_2]^+$	268	95
$[VF(C_5H_7O_2)(C_4H_4O_2)]^+$	253	84
$[VF(C_5H_7O_2)(C_3H_5O)]^+$	226	32
$[VF(C_5H_7O_2)OH]^+$	186	90
$[VF(C_5H_7O_2)]^+$	169	100
$[VF(C_4H_4O_2)]^+$	154	26
$[VF(C_3H_5O)]^+$	127	22
$[VF]^+$	70	25

Metastable Transitions

*m/z**			
obsd	calcd	process	fragment lost
238.8	238.84	268 → 253	CH_3
190.7	190.58	268 → 226	CH_2CO
129.2	129.09	268 → 186	C_5H_6O
112.8	112.89	253 → 169	$C_4H_4O_2$
140.4	140.33	169 → 154	CH_3
31.9	31.82	154 → 70	$C_4H_4O_2$

arising due to the presence of fluoride coordinated[8] to the vanadium center. The IR spectrum also exhibited bands characteristic for $N_2H_5^+$.[9] Thus, on the basis of the results of chemical analyses and IR spectral studies, the formula $N_2H_5VOF_3$ has been assigned to the compound.

$$2V_2O_5 + 5N_2H_4{\cdot}H_2O + 12HF \rightarrow 4N_2H_5VOF_3 + N_2 + 11H_2O$$

Evidence for the formation of dinitrogen (see Experimental Section) lends support to the above equation. The molar conductance of the compound was found to be 130 Ω^{-1} cm^2 mol^{-1}, suggesting a 1:1 electrolytic nature of the compound. The room-temperature magnetic moment showed it to be a vanadium(IV) case. The electronic spectrum of the compound exhibited two d–d transition bands at 12000 and 16000 cm^{-1}, which have been assigned to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions, respectively.[7] The spectral pattern indicates a C_{4v} symmetry of the complex species, in solutions, which it might have achieved by gaining an F^- ligand at the vacant site in the equatorial plane through fluoride exchange between two contiguous VOF_3^- ions. Although the results support the mononuclear formulation of the complex species, chances of a polymeric structure through a weak V–F–V or a V–O–V interaction cannot be totally ruled out.

The blue hydrazonium oxytrifluorovanadate(IV), $N_2H_5VOF_3$, reacts further with an excess of acetylacetone under mild conditions to give ultimately the blue-green crystalline bis(acetylacetonato)fluorovanadium(III), VF(acac)$_2$. The reaction was rather facile and gave a very high yield of the product. It is interesting to note that although acetylacetone (acacH) is capable of reducing Mn^{7+} to Mn^{3+},[10] Cr^{6+} to Cr^{3+},[11] or Ni^{3+} to Ni^{2+} [12] with acacH being oxidized to $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CHCH(CH_3CO)_2$,[12] it alone cannot reduce V^{4+}.[13] In the present case, isolation of $\alpha,\alpha,\beta,\beta$-tetraacetylethane, after VF(acac)$_2$ is separated from the reaction solution, suggests the possibility of acacH acting as a reducing agent. However, the importance of $N_2H_5^+$ cannot be underestimated though we do not have any direct evidence of its oxidation.

Blue-green bis(acetylacetonato)fluorovanadium(III), $VF(C_5H_7O_2)_2$, is stable for prolonged periods and can be stored in a sealed polyethylene capsule. The compound melts at 246–248 °C and is soluble in many common organic solvents. The oxidimetric titration with standard potassium permanganate shows that vanadium in the compound has an oxidation state of +3, which was further confirmed by magnetic susceptibility measurement. The room-temperature magnetic moment was found to be 2.77 μ_B, which conforms to those reported in the literature for trivalent vanadium compounds.[14] The infrared spectrum of the compound exhibits a pattern typical for the presence of coordinated acetylacetonate (acac$^-$) bonded to the V^{3+} center in a bidentate chelated manner.[10–12,15] Besides this, there is a strong band at 470 cm^{-1}, which has been assigned to ν_{V-F}.[8] The somewhat broad nature of the band indicates the possibility of a weak V–F···V interaction, and this leads us to believe that in the solid state VF(acac)$_2$ may have a hexacoordinated structure through a weak V–F···V bridging.

In order to obtain further information, we recorded mass spectra of the compound using a direct-insertion technique. The compound gave a well-developed spectrum at 150 °C with the highest *m/z* signal at 268 owing to the molecular ion $VF(C_5H_7O_2)_2^+$, suggesting that in the vapor state the compound is only monomeric, and the most dominant peak at *m/z* 169 assigned to $VF(C_5H_7O_2)^+$, with the major fragmentation pathway being $VF(C_5H_7O_2)_2^+ \rightarrow VF(C_5H_7O_2)(C_4H_4O_2)^+ \rightarrow VF(C_5H_7O_2)^+ \rightarrow VF(C_4H_4O_2)^+ \rightarrow VF^+$. The metastable peaks (Table I) at *m/z** 238.8, 140.4, 112.8, and 31.9 support the fragmentation pattern.

Thus, it appears from our present work that a trivalent vanadium compound, VF(acac)$_2$, can be synthesized from pentavalent vanadium under suitable conditions. The compound may have a hexacoordinated polymeric structure, through a weak V–F···V interaction, in the solid state; however, in the vapor state, VF(acac)$_2$ definitely exists in its monomeric form.

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Registry No. $VF(C_5H_7O_2)_2$, 90461-85-1; $N_2H_5VOF_3$, 90461-86-2.

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